

## Total energies in the tight-binding theory

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The density-functional theory of interaction between closed-shell atoms is simplified sufficiently to be carried out analytically. The resulting form is  $V_0(d) = -\eta_0 \epsilon_p \mu d \exp(-5\mu d/3)$ , where the valence  $p$ -state energy is related to  $\mu$  by  $\epsilon_p = -\hbar^2 \mu^2/2m$ . In universal-parameter tight-binding theory of ionic crystals a band-structure energy is added, but no Madelung energy.  $\eta_0$  is adjusted from its theoretical value of 71 to give the correct equilibrium spacing for the potassium halides, giving  $\eta_0 = 44, 86, 103,$  and  $146$  for  $2p, 3p, 4p,$  and  $5p$  anions, respectively. Then using average values of  $\mu$  based upon Herman-Skillman term values the equilibrium spacing, cohesive energy, and elastic constants are predicted for the monovalent, divalent, and trivalent compounds in the rocksalt structure. Such a theory based upon tight-binding energies rather than Madelung energies provides an alternative to the Born theory. It is of comparable accuracy but has much wider applicability. The theory also predicts an approximate equality between the band gap and the cohesive energy per ion pair for the alkali halides and between twice the band gap and the cohesive energy for their divalent counterparts, in reasonable accord with experiment. By identifying the overlap interaction in covalent solids with nonorthogonality terms in tight-binding theory it is shown that direct application of the closed-shell theory to covalent solids underestimates the kinetic-energy term by a factor of  $2^{2/3}$ . Making this correction to the earlier calculations for Si and Ge by Harrison and Sokel brings them into reasonable accord with experiment. This overlap interaction is then approximated by the same analytic form as for closed-shell systems but based upon hybrid, rather than  $p$ -state, parameters. The coefficient  $\eta_0$  is adjusted, from its theoretical value of 47, to 46 for C, 57 for Si, 61 for Ge, and 73 for Sn in order to fit the observed atomic spacing. The resulting overlap interaction plus the bonding energy then gives direct predictions of the cohesion and bulk modulus for these elements, reproducing the observed trends. The theory is extended to polar semiconductors by again identifying the overlap interaction with the nonorthogonality terms of tight-binding theory. This suggests a nonorthogonality  $S = (1/2)\alpha_c^h$ , where  $\alpha_c^h$  is the hybrid covalency of the compound, and a replacement of  $\eta_0$  by  $\eta_0 \alpha_c^h$  for the overlap interaction of the polar semiconductors. The latter leads to reasonable predictions, without further parameters, of the equilibrium spacing, cohesion, and bulk modulus for these systems. The dependence of  $S$  on covalency is *not* supported by detailed calculation. The identification of the overlap interaction with the nonorthogonality terms also suggests an approximate relation between the average of the  $\mu_i$ 's, based upon the hybrid energies, and the equilibrium spacing  $d = 3/\bar{\mu}_h$ , in rough accord with experiment. Finally, the total energy is reconsidered using extended Hückel theory. It is seen that the approximations in the two theories can be related and the parameters from the two theories identified with each other though their formulation is much different. By evaluating the nonorthogonality  $S$  of extended Hückel theory, using the same approximations which were used here in the evaluation of the overlap interaction, we verify that it leads to values and  $d$  dependence of the overlap and of interatomic matrix elements consistent with those of universal-parameter tight-binding theory. It leads also to a similar form for, and value of, the overlap interaction.

### I. INTRODUCTION

Elementary tight-binding theory has been used to successfully predict the dielectric and bonding properties of ionic and covalent solids.<sup>1</sup> The volume dependence of the energy in terms of local orbitals, however, has required extensive computation for the ionic solids<sup>2</sup> and the attempt to extend the method to covalent solids was unsuccessful<sup>3</sup>; the introduction of an empirical repulsive interaction between atoms in the covalent solids has been required.<sup>1</sup> We seek to rectify these difficulties in the analysis here.

### II. THE LCAO FORMULATION

We begin by reformulating the total energy in terms of linear combinations of atomic orbitals. The basic approximation of this linear combination of atomic orbitals (LCAO) method is the

assumption that the one-electron eigenstates can be adequately written as a sum of free-atom orbitals. For simplicity of notation we consider a linear combination of an atomic orbital  $|\alpha\rangle$  on one atom and one  $|\beta\rangle$  on a neighboring atom:

$$|\psi\rangle = u_{i\alpha}|\alpha\rangle + u_{i\beta}|\beta\rangle, \quad (1)$$

though the analysis can immediately be generalized (see Sec. V) to solids with  $|\psi_i\rangle = \sum_{\alpha} u_{i\alpha}|\alpha\rangle$ . The  $u_{i\alpha}$  and  $u_{i\beta}$  are constant coefficients. The one-electron Hamiltonian of the system is approximated by the kinetic energy plus the sum of free-atom potentials for the two atom in the following:

$$H = \frac{-\hbar^2}{2m} \nabla^2 + v_{\alpha} + v_{\beta}. \quad (2)$$

With these two approximations the one-electron energies can be written

$$\frac{\langle \psi_i | H | \psi_i \rangle}{\langle \psi_i | \psi_i \rangle} = \frac{u_{i\alpha}^* u_{i\alpha} (\epsilon_\alpha + \delta\epsilon_\alpha) + u_{i\beta}^* u_{i\beta} (\epsilon_\beta + \delta\epsilon_\beta) + (u_{i\alpha}^* u_{i\beta} + u_{i\beta}^* u_{i\alpha}) H_{\alpha\beta}}{u_{i\alpha}^* u_{i\alpha} + u_{i\beta}^* u_{i\beta} + (u_{i\alpha}^* u_{i\beta} + u_{i\beta}^* u_{i\alpha}) S}, \quad (3)$$

with  $\epsilon_\alpha = \langle \alpha | -\hbar^2 \nabla^2 / 2m + v_\alpha | \alpha \rangle$ , the free-atom energy for state  $|\alpha\rangle$ , and  $\epsilon_\beta$  the free-atom energy for  $|\beta\rangle$ .  $\delta\epsilon_\alpha = \langle \alpha | v_\beta | \alpha \rangle$  is the shift in that energy due to the second atom and similarly  $\delta\epsilon_\beta = \langle \beta | v_\alpha | \beta \rangle$ . The matrix element  $H_{\alpha\beta} = \langle \alpha | H | \beta \rangle$  is the coupling between the states and  $S = \langle \alpha | \beta \rangle$  is the overlap. We shall see that  $S$  is expected to be approximately  $\frac{1}{2}$  in covalent solids. We have normalized the atomic states  $\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1$ .

A variational method is used to obtain the states, taking the derivative of Eq. (3) with respect to  $u_{i\alpha}$  and  $u_{i\beta}$  equal to zero.<sup>4</sup> If this is actually carried out with real atomic orbitals and atomic potentials the calculation is called "first-principles LCAO theory." If the parameters  $\epsilon_\alpha$ ,  $\epsilon_\beta$ ,  $H_{\alpha\beta}$ , etc., are obtained in some other way the calculation is usually called "tight-binding theory." We follow the latter approach but retain the LCAO interpretation of the parameters in deriving the total energy. Before doing that it is convenient to define new parameters:

$$V_2 = |H_{\alpha\beta}| / (1 - S^2), \quad (4)$$

$$V_3 = (\epsilon_\alpha + \delta\epsilon_\alpha - \epsilon_\beta - \delta\epsilon_\beta) / (1 - S^2)^{1/2}.$$

Then the variational solution takes the simple form<sup>4</sup>

$$\frac{\langle \psi_i | H | \psi_i \rangle}{\langle \psi_i | \psi_i \rangle} = \frac{\epsilon_\alpha + \epsilon_\beta}{2} \pm (V_2^2 + V_3^2)^{1/2} + \frac{\delta\epsilon_\alpha + \delta\epsilon_\beta}{2} + SV_2. \quad (5)$$

The minimum, or bonding, energy is obtained with the minus. The state orthogonal to it, the antibonding state, has the plus sign. In a closed-shell system each is occupied by an electron with spin up and one with spin down.

We return in Sec. IV to the choice of parameters, but first note that we cannot obtain the total energy simply by adding the energies of the occupied states. The term  $\delta\epsilon_\alpha$  contains the potential energy of interaction between the electrons in  $|\alpha\rangle$  and the electrons in  $|\beta\rangle$  and that same interaction is included again in  $\delta\epsilon_\beta$ . In the one-electron approximation all such electron-electron interactions are counted twice and must be subtracted once in evaluating the total energy. In addition the Coulomb interaction between nuclei (or ion cores) must be added. The sum of one-electron energies, so corrected, gives the total energy.

Note that for a closed-shell system the terms  $\pm (V_2^2 + V_3^2)^{1/2}$  sum to zero and the energy, relative to the free-atom energies  $\epsilon_\alpha + \epsilon_\beta$ , is given by a

series of potential energies and the terms  $SV_2$ . The last term includes the extra electronic kinetic energy associated with compression of the electron gas due to overlapping the two atomic charge distributions. Note that if the two orbitals were orthogonal ( $S=0$ ), they could both be occupied and there would be no extra kinetic energy. The construction of orthogonal orbitals inevitably yields extra kinetic energy which is the origin of the forces which prevent the collapse of matter under the mutual Coulomb interactions. The identification of the  $SV_2$  term with the excess kinetic energy will be particularly important when we discuss open-shell systems.

### III. DENSITY-FUNCTIONAL THEORY FOR CLOSED-SHELL SYSTEMS

Nikulin and Tsarev<sup>5</sup> and Gordon and Kim<sup>2</sup> have developed an approximate method for evaluating the total energy of interaction between inert-gas atoms and closed-shell ions. In this method the different terms in the potential energy—the potential energy of interactions between ions, between electrons and ions, and among electrons—as well as the excess kinetic energy were estimated at each point in terms of the electron density at that point using formulas for the energy of a free-electron gas of uniform density. The electron density itself was approximated by a direct superposition of the free-atom densities obtained in the Hartree-Fock approximation. There are basic arguments<sup>6</sup> which suggest that this might be a good approximation and it has turned out to be quantitatively very accurate in a wide variety of closed-shell systems.<sup>2</sup> We may think of the method as an approximate evaluation of the various potential-energy and kinetic-energy contributions discussed in the preceding section (which in turn were an approximation to the real problem). Again, the term  $\pm (V_2^2 + V_3^2)^{1/2}$  in Eq. (5) does not enter in closed-shell systems but all other terms are estimated. The evaluation of the various terms in the energy requires a numerical integration over the region of the overlapping charge distributions and leads to a tabulated "overlap interaction" between each pair of closed-shell atoms.

We seek here an approximate evaluation of the overlap interaction which can be carried out analytically. The purpose is not just to avoid a somewhat tedious numerical procedure, but to provide analytic formulas for the interaction which can then be used to describe a wide variety

of systems without recalculation. It also allows general calculations of properties in terms of these formulas and clarifies the nature of the dominant contributions. The basic approach is to make a series of approximations which become increasingly accurate at large spacing between the atoms; that is, we seek the asymptotic form of the overlap interaction and shall then assume that this form remains appropriate near the observed internuclear spacings between atoms. We test at each step how accurate these approximations are. We begin with a discussion of the electron density.

#### A. The charge density

In the Hartree-Fock calculation of the electronic structure of a neutral atom the potential seen by each electron—at sufficiently large distance—approaches simply  $-e^2/r$ . The asymptotic form for the solution of the radial Schrödinger equation for this case is readily obtained and is given by

$$R_l(r) \sim r^\gamma e^{-\mu r}, \quad (6)$$

where  $\mu$  is related to the term value by

$$\hbar^2 \mu^2 / (2m) = -\epsilon_l \quad (7)$$

and  $\gamma = (e^2 m) / (\hbar^2 \mu) - 1$ . Note that the form of the result does not depend upon  $l$ . If the atomic energy happened to be  $-13.6$  eV, one rydberg, then  $\gamma$  would equal zero. The influence of the  $r^\gamma$  factor is sufficiently small and the energies of interest near enough to a rydberg that we shall make the approximation  $\gamma=0$ . It would not be difficult to retain that factor but it would complicate the form of the results more than seems justified.

The valence  $p$  states in most atoms are only about half as deep as the valence  $s$  states so the corresponding  $\mu$  value is 30% smaller and the charge density at large distances is thus dominated by the  $p$  states; the fact that there are three times as many contributes to this dominance and it may readily be confirmed by examination of any atomic structure tables. Thus we approximate the electron density at large distances by the form  $e^{-2\mu r}$ , and we normalize it to a total of six  $p$  electrons in the following:

$$n(r) = 6\mu^3 e^{-2\mu r} / \pi. \quad (8)$$

This is to be used in place of the Hartree-Fock densities used by Gordon and Kim. Note that we underestimate the normalization constant since the real atomic orbital drops below the asymptotic form, Eq. (6), at small  $r$ . The reduction in density is called the "orthogonalization hole" or "depletion hole" in pseudopotential theory. Indeed the error increases with increasing row

in the Periodic Table. We will ultimately correct for this by an empirical scaling, but now proceed without empirical corrections.

A plot of this approximate density for argon, along with the Hartree-Fock density from Fisher<sup>7</sup> is shown in Fig. 1. The approximation is very good over much of the range of interest and could be improved still further by a constant scale factor. We use it throughout our analysis; the electron density from Eq. (8) is superimposed for two neighboring closed-shell atoms and we proceed to evaluate the change in kinetic and potential energies.

#### B. The kinetic energy

The average kinetic energy  $\langle \hbar^2 k^2 / 2m \rangle$  for a free-electron gas of density  $n$  is readily evaluated and is

$$\epsilon_{KE}(n) = \frac{3}{5} (3\pi^2)^{2/3} \frac{\hbar^2 n^{2/3}}{2m}. \quad (9)$$

Thus the local-density approximation to the total kinetic energy is simply  $\int d^3r \epsilon_{KE}(n(\vec{r})) n(\vec{r})$ . Writing the electron density [Eq. (8)] from the two atoms as  $n_1(r_1)$  and  $n_2(r_2)$  we find the contribution to the overlap interaction

$$V_0^{KE} = \frac{3}{5} (3\pi^2)^{2/3} \frac{\hbar^2}{2m} \int d^3r [(n_1 + n_2)^{5/3} - n_1^{5/3} - n_2^{5/3}]. \quad (10)$$

To evaluate the integral we take a cylindrical coordinate system with origin at the midpoint between atoms. Then  $r_2 = [(d/2 - z)^2 + \rho^2]^{1/2} = \frac{1}{2}d - z + \rho^2/d$  plus terms of higher order in  $z/d$  and  $\rho^2/d^2$ . After using a little algebra Eq. (10) becomes

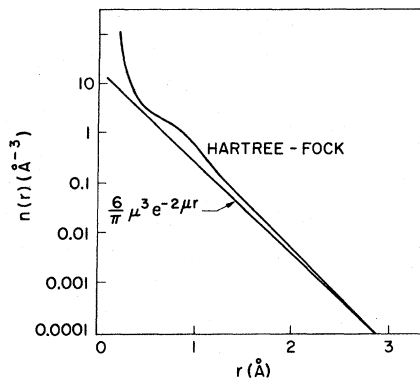


FIG. 1. The electron density in argon from the normalized asymptotic form, compared with the density obtained from a Hartree-Fock calculation by Fisher (Ref. 7).

$$\begin{aligned}
V_0^{\text{KE}} &= \frac{3}{5} (3\pi^2)^{2/3} \left(\frac{6}{\pi}\right)^{5/3} \frac{\hbar^2 \mu^5}{2m} e^{-5\mu d/3} \int_0^\infty e^{-10\mu\rho^2/3d} 2\pi \rho d\rho \int_{-\infty}^\infty [(e^{-2\mu z} + e^{2\mu z})^{5/3} - e^{-10\mu z/3} - e^{10\mu z/3}] dz \\
&= \frac{3}{5} (3\pi^2)^{2/3} \left(\frac{6}{\pi}\right)^{5/3} \frac{\hbar^2 \mu^2}{2m} e^{-5\mu d/3} \frac{3\pi\mu d}{10} K\left(\frac{5}{3}\right), \tag{11}
\end{aligned}$$

where

$$K(\alpha) = \int_0^\infty dx [(e^{-x} + e^x)^\alpha - e^{-\alpha x} - e^{\alpha x}]. \tag{12}$$

$K(\frac{5}{3})$  was obtained as 4.45 by numerical integration. Equation (11) becomes

$$V_0^{\text{KE}} = -70.8 \epsilon_\mu \mu d e^{-5\mu d/3}. \tag{13}$$

It is given in Table I for the argon  $p$  state energy of  $-16.08$  eV, along with Gordon and Kim's values obtained from numerical integration of Hartree-Fock electron densities for argon-argon interactions. Our result is small by a factor of order two but note that it is not a fit to their results but an elementary approximate first-principles calculation. It will be informative although it is not so accurate. We proceed to other terms.

#### C. Exchange energy

The calculation of exchange energy is very similar. The exchange energy per electron in a uniform electron gas is  $-(3\pi^2)^{1/3} 3e^2 n^{1/3} / (4\pi)$  so the contribution to the overlap interaction is

$$\begin{aligned}
V_0^x &= -\frac{3}{4\pi} (3\pi^2)^{1/3} e^2 \int d^3r [(n_1 + n_2)^{4/3} - n_1^{4/3} - n_2^{4/3}] \\
&= -\frac{3}{4\pi} (3\pi^2)^{1/3} e^2 \mu \left(\frac{6}{\pi}\right)^{4/3} \frac{3\pi}{8} K\left(\frac{4}{3}\right) \mu d e^{-4\mu d/3}. \tag{14}
\end{aligned}$$

Numerically integrating Eq. (12) leads to  $K(\frac{4}{3}) = 1.323$  and

$$V_0^x = -2.728 e^2 \mu \mu d e^{-4\mu d/3}. \tag{15}$$

This is also tabulated for argon along with the Gordon-Kim results.

#### D. Coulomb energy

The calculation of the Coulomb energy is slightly different. The potential (times  $-e$ ) due to a neutral atom with electron density given by Eq. (8) is

$$V(r) = -6e^2(1 + \mu r)e^{-2\mu r}/r, \tag{16}$$

which may be immediately verified using Poisson's equation. For large separations we retain only the second term ( $\mu r$ ) and the Coulomb energy becomes

$$V_0^{\text{CO}} = +36\mu e^2 \mu e^{-2\mu d} - \frac{36e^2\mu}{\pi} \mu^3 \int e^{-2\mu r_1} e^{-2\mu r_2} d^3r. \tag{17}$$

The integral can be performed exactly using ellipsoidal coordinates to obtain

$$\pi(2\mu)^{-3}(1 + 2\mu d + 4\mu^2 d^2/3) \exp(-2\mu d).$$

Then

$$V_0^{\text{CO}}(d) = -6e^2\mu(\mu d)^2 e^{-2\mu d} \tag{18}$$

plus terms of lower order in  $\mu d$ . This is also tabulated in Table I along with the Gordon-Kim values.

#### E. Correlation energy

The remaining terms in the energy of an electron gas, beyond the kinetic energy, Coulomb energy, and exchange energy, are called the correlation energy. Gordon and Kim used values calculated for the uniform gas from the high-density limit and from the low-density limit and

TABLE I. Contributions to the overlap interaction in argon, calculated here and by Gordon and Kim (GK) (Ref. 2).

$d$ Å	$V_0^{\text{KE}}$ (eV)		$V_0^x$ (eV)		$V_0^{\text{CO}}$ (eV)	
	Eq. (13)	GK	Eq. (15)	GK	Eq. (18)	GK
0.529	$2.02 \times 10^2$	$5.65 \times 10^2$	$-2.06 \times 10$	$-6.34 \times 10$	$-2.39 \times 10$	$1.95 \times 10^2$
1.058	$6.61 \times 10$	$1.54 \times 10^2$	$-9.67$	$-2.49 \times 10$	$-1.085 \times 10$	$-6.63 \times 10$
1.587	$1.62 \times 10$	$3.47 \times 10$	$-3.41$	$-8.00$	$-2.78$	$-1.54 \times 10$
2.116	3.53	6.99	$-1.07$	$-2.26$	$-5.62 \times 10^{-1}$	$-2.48$
2.645	$7.22 \times 10^{-1}$	1.29	$-3.13 \times 10^{-1}$	$-5.89 \times 10^{-1}$	$-9.99 \times 10^{-2}$	$-3.47 \times 10^{-1}$
3.174	$1.42 \times 10^{-1}$	$2.28 \times 10^{-1}$	$-8.82 \times 10^{-2}$	$-1.47 \times 10^{-1}$	$-1.64 \times 10^{-2}$	$-4.60 \times 10^{-2}$
3.703	$2.70 \times 10^{-2}$	$3.93 \times 10^{-2}$	$-2.42 \times 10^{-2}$	$-3.57 \times 10^{-2}$	$-2.54 \times 10^{-3}$	$-6.21 \times 10^{-3}$
4.232	$5.04 \times 10^{-3}$	$6.81 \times 10^{-3}$	$-6.48 \times 10^{-3}$	$-8.66 \times 10^{-3}$	$-3.77 \times 10^{-4}$	$-9.27 \times 10^{-4}$
4.761	$9.27 \times 10^{-4}$	$1.23 \times 10^{-3}$	$-1.71 \times 10^{-3}$	$-2.13 \times 10^{-3}$	$-5.42 \times 10^{-5}$	$-1.60 \times 10^{-4}$
5.290	$1.68 \times 10^{-4}$	$2.39 \times 10^{-4}$	$-4.46 \times 10^{-4}$	$-5.47 \times 10^{-4}$	$-7.62 \times 10^{-6}$	$-3.15 \times 10^{-5}$

interpolated for intermediate densities. We cannot obtain analytic forms for the integrals over these, even with our approximate electron density. The treatment of these terms is less convincing than the others in any case and they are not important in the ionic and covalent solids which are of particular interest here so we have not evaluated them. For the inert gases the correlation energy produces almost all of the binding of the solid and brings the spacing, according to the Gordon-Kim calculation, down close to the observed value.

#### F. Comparison of contributions

A consideration of Table I indicates that the approximate analytical calculations scale rather well with detailed numerical results over many decades. For our purposes the most interesting range is near  $d=3\text{ \AA}$ , the spacing of KCl, which is isoelectronic with  $\text{Ar}_2$ . In this region the kinetic energy is seen to be the dominant term, although the exchange energy is far from negligible. A scaling of our results will be needed in any case and since the form of the two terms is so close [see Eqs. (13) and (15)] it is reasonable to take the total overlap interaction to be of the form of the kinetic energy term and introduce the appropriate scaling there. This is also physically satisfying since, as we indicated in the preceding section, it is the kinetic energy which prevents the collapse of the system and we are to introduce additional attractive terms [such as the  $-(V_2^2 + V_3^2)^{1/2}$ ] which dominate the cohesion of the system. Thus we regard Eq. (13) as an approximate first-principles calculation of the overlap interaction but allow the scale factor in front,  $\eta_0=70.8$ , to be adjusted to correct for the errors arising from our approximation, an approach similar to that which we use for obtaining tight-binding parameters.

#### IV. UNIVERSAL TIGHT-BINDING PARAMETERS

It is well known that the energy bands of the covalent semiconductors can be rather well described on the basis of valence  $s$  and  $p$  states on each atom and nearest-neighbor tight-binding matrix elements.<sup>1</sup> It has also long been known that there is strong resemblance between the bands and free-electron bands. By requiring that the two approaches give the same results at the principal band energies at  $\Gamma$  and  $X$ , Froyen and Harrison,<sup>8</sup> derived formulas in terms of the internuclear distance for the interatomic matrix elements and for  $\epsilon_p - \epsilon_s$  as follows:

$$V_{ll'm} = \eta_{ll'm} \hbar^2 / (md^2), \quad (19)$$

with, for example,  $\eta_{ss\sigma} = -9\pi^2/64$ . Comparison

with the known bands of the tetrahedral semiconductors indicates that with minor adjustments of the dimensionless coefficients  $\eta_{ll'm}$  ( $\eta_{ss\sigma} = -1.40$ ,  $\eta_{sp\sigma} = 1.84$ ,  $\eta_{pp\sigma} = 3.24$ ,  $\eta_{pp\pi} = -0.81$ ) these interatomic matrix elements give very good valence bands and tolerable conduction bands for C, Si, Ge, and Sn; in fact, Eq. (19) was given earlier<sup>9</sup> as an empirical form for the matrix elements obtained from study of the known bands. Equation (19) gives the variations under pressure as well as the variations from material to material. It was found, however, that the corresponding formula for the energy difference  $\epsilon_p - \epsilon_s$  was in agreement only for Sn and that atomic term values should be used for all if good results are to be obtained. Values given by Herman and Skillman<sup>10</sup> have proven adequate. It was further found from a study of the bands of polar semiconductors that use of atomic term values for the two atom types and the same interatomic matrix elements, Eq. (19), gave a good account of the energy bands also for those semiconductors.<sup>1,9</sup> Applications of the same approach to ionic crystals, such as alkali halides, suggested again that use of atomic term values and Eq. (19) (with the same coefficients  $\eta_{ll'm}$ ) gave good representations of the electronic structure.<sup>1</sup> Again, only a *minimal basis set* of atomic orbitals is used, those that are occupied or partially occupied in the free atom. Thus we have values for all of the tight-binding parameters which are needed for the analysis of the total energy.

In addition, a very important and surprising postulate follows from requiring that we be internally consistent. We have noted that *atomic* term values are to be used, not free-ion values with Madelung corrections as we might have anticipated for alkali halides, for example. This is consistent with experiment; the difference in term values for the potassium  $s$  state and the chlorine  $p$  state, 8.1 eV, is in good agreement with the observed band gap of 8.4 eV in KCl. This means that the Madelung shift of 16 eV of the difference between the two levels very nearly cancels the difference between free-ion and free-atom term values; it is fortunate that we do not need to calculate these two competing shifts individually. This is also consistent with the known fact that in the equilibrium structure the charge density corresponding to superimposed free atoms very nearly equals that corresponding to superimposed free ions.<sup>11</sup> In some sense our choice of these universal tight-binding parameters and atomic term values means we have selected "atomic orbitals" which have this property though we never use those orbitals explicitly. This would suggest that we should also not include a

Madelung electrostatic energy in the calculation of total energy when we are near the equilibrium spacing. We simply sum the electronic energies and make the appropriate corrections as suggested in Sec. II.

This neglect of Madelung energies is not inconsistent with the fact that the total energy of an ionic crystal can accurately be calculated as the energy to form free ions at infinite separation minus the electrostatic energy gained in bringing them together in the crystal. We may imagine that in the construction of the crystal the electrons slightly rearrange as the ions come into contact, forming neutral atoms, but with only a small change in energy in doing it. An alternative path from the atom to the crystal would bring neutral atoms together, with no gain in electrostatic energy, and the entire formation energy is obtained when the electronic states of the crystal are formed as the atoms come into contact. It is simply two different paths between the same end points and must give the same formation energy.

It may be of interest that this postulate that the sums of electronic energies, not the Madelung energy, were to be added to the overlap interaction to obtain the observed spacing arose initially not from this internal consistency argument but from the empirical finding that when the Madelung energy was used and  $\eta_0$  adjusted to give correct spacings the fitted values were not simple; a new value of  $\eta_0$  needed to be fitted for each compound.<sup>12</sup> Only when the sums of band energies were used did the fitted values become simple as we see in the following section.

## V. IONIC COMPOUNDS

We must first generalize the calculation of electronic states, given in Sec. II, to the rocksalt structure. Instead of only two orbitals we include the minimal basis set. For the alkali halides or their divalent counterparts, this includes the valence  $s$  state on the metallic atom and the valence  $s$  and  $p$  states on the nonmetallic atom. The  $s$  state on the nonmetallic atom is sufficiently deep that it is a good approximation to neglect it and this simplifies the calculation considerably. Each electronic state may be associated with a wave number in the Brillouin zone and the four energy eigenvalues associated with each wave number are obtained by diagonalizing a four-by-four Hamiltonian matrix. In fact, when three levels of the same energy ( $\epsilon_p$ ) are coupled to a single level (of energy  $\epsilon_s$ ), two eigenvalues are given exactly by  $\epsilon_p$  and the remaining two are obtained from the solution of a quadratic equation, giving results of just the form given in Sec. II.

However, these two eigenvalues depend upon the wave number and we must sum the occupied levels over all wave numbers in the Brillouin Zone.

### A. The special points method

Baldereschi<sup>13</sup> has suggested an approximate method of obtaining this sum by carefully selecting a single wave number which is representative of the entire Brillouin zone and has given a procedure for selecting that point. We use that method but, interestingly enough, find it unnecessary to follow his selection procedure. The solution for the eigenvalues at the special point will be of the form of Eq. (5) and  $V_3$  will equal  $\frac{1}{2}(\epsilon_s - \epsilon_p)$  and  $V_2$  will be proportional to  $V_{sp\sigma}$ , but we do not know immediately the proportionality constant; it does depend upon the wave number of the selected special point. However, the same procedure remains valid when  $V_2$  is very much smaller than  $V_3$  so we may simply require that the coefficient be such that the shift in energy to second order in  $V_2$ , that is,  $\frac{1}{2}V_2^2/V_3$  for the upper level, be equal to the value  $nV_{sp\sigma}^2/(\epsilon_s - \epsilon_p)$  if each ion has  $n$  nearest neighbors, obtained with second-order perturbation theory. It follows that  $V_2^2 = nV_{sp\sigma}^2$ , in agreement with the result obtained with the Baldereschi point for the face-centered-cubic Brillouin zone appropriate to both rocksalt ( $n=6$ ) and zinblende ( $n=4$ ) structures. The equivalence is rather astounding in view of the somewhat *ad hoc* procedure used to obtain the special point for this structure but may be taken as additional justification for both approaches.

This coupling raises the energy of a single band and lowers the energy of another. Since the lowered level is doubly occupied the lowering in energy per ion pair due to the coupling is

$$\begin{aligned} \delta E_{\text{band}} = & -2(V_2^2 + V_3^2)^{1/2} + 2V_3 \\ = & -[(\epsilon_s - \epsilon_p)^2 + 4nV_{sp\sigma}^2]^{1/2} + (\epsilon_s - \epsilon_p). \end{aligned} \quad (20)$$

(Note that this vanishes if the coupling  $V_{sp\sigma}$  vanishes and approaches the second-order expression for the lower value when  $V_{sp\sigma}$  is small.) To obtain the energy relative to that for free atoms for the alkali halides we must subtract an additional  $(\epsilon_s - \epsilon_p)$ , the energy gain in transferring a single electron from the alkali  $s$  state to the halogen  $p$  state in the absence of any coupling. For the divalent counterparts this energy is subtracted twice for the two electrons, and for the trivalent compounds an additional  $\epsilon_d - \epsilon_p$  is subtracted for the third electron transferred from the metal. The correction terms for electron-electron interaction counted twice (discussed in Sec. II) and the interaction between nuclei are ex-

licitly included in the overlap interaction. Any effects of double counting on the band energies are assumed to be absorbed in the selection of the parameters  $V_{11'm}$ .

### B. The overlap interaction

The overlap interaction as calculated in Sec. III (though not as calculated by Gordon and Kim) assumed the two interacting atoms were identical;  $\mu$  was calculated using Eq. (7) and the common  $p$ -state energy. If we compare the interaction for KCl with that for  $\text{Ar}_2$ , which is isoelectronic with it, we observe by symmetry that any change in the overlap interaction must be quadratic in the difference in  $p$ -state energies. Thus it is a plausible approximation to use the average  $\bar{\mu} = \frac{1}{2}(\mu_1 + \mu_2)$  of the values obtained for each ion and to replace  $\epsilon_p$  in Eq. (13) by  $\hbar^2 \mu_1 \mu_2 / (2m)$ . This form will in fact be justified using extended Hückel theory (EHT) in Sec. VII. If we chose, we could then obtain an empirical  $\eta_0$  to replace the factor 70.8 in Eq. (13) by adjusting it to yield the observed internuclear spacing for each compound. This procedure was carried out by Brock.<sup>12</sup> He found that  $\eta_0$  only depended strongly upon the principal quantum number of the  $p$  state on the nonmetallic ion, the anion.

It may not be surprising that the principal dependence is upon the larger ion. The largest contribution to the extra kinetic energy of Eq. (11) comes from integration in the region of the smaller ion and is scaled directly by any re-normalization of the electron density of the larger ion due to an orthogonalization hole at the center of that large ion. On the other hand, the re-normalization of the electron density on the smaller ion tends to be canceled by the decreased electron density of the orthogonalization itself. It should nevertheless be regarded as an empirical finding since the adjustment of  $\eta_0$  is expected also to correct for our neglect of the exchange energy of Eq. (15). This empirical finding allows us to define four universal values of  $\eta_0$  to be associated with  $2p$ ,  $3p$ ,  $4p$ , and  $5p$  valence shells and these may be used for all ionic compounds.

A second problem arises from the presence of two different ion sizes. When the ions are identical the contribution of second-neighbor interactions in the rocksalt structure is negligible because the spacing  $d$  entering  $\exp(-5\mu d/3)$  is larger by  $2^{1/2}$ . This increased length between anions is partly canceled by the smaller value of  $\mu$  and we must include second neighbors also. There is no difficulty in doing this and the  $\eta_0$  value we use is that for the anion. Then for crystals in the rocksalt structure the total effect per ion pair of the overlap interaction between the anion

and its six cation neighbors [ $6V_0(d)$  per anion] and its twelve anion next-nearest neighbors [ $12V_0(\sqrt{2}d)/2$  per anion] is

$$\delta E_{\text{overlap}} = 6\eta_0 \frac{\hbar^2}{2m} (\bar{\mu}^3 d e^{-5\mu d/3} + 2^{1/2} \mu^3 d e^{-5\sqrt{2}\mu d/3}), \quad (21)$$

where  $\eta_0$  and  $\mu$  are associated with the anion and  $\bar{\mu}$  is the average of the anion and cation values.  $d$  is the nearest-neighbor distance and  $2^{1/2}d$  is the second-neighbor distance.

The total crystal energy, relative to that of separated neutral atoms, is the sum of Eqs. (20) and (21) [with additional terms  $\epsilon_s - \epsilon_p$  and  $\epsilon_d - \epsilon_p$  for polyvalent compounds, as indicated following Eq. (20)]. Given values for  $\eta_0$  we may directly predict  $d$ , the heat of atomization, and the bulk modulus for any compound in the rocksalt structure.

We have chosen to determine the four  $\eta_0$  values to yield the observed internuclear distance  $d$  in KF, KCl, KBr, and KI. This gives values of

$$\eta_0 = 44 \text{ for } 2p \text{ anions, } 86 \text{ for } 3p \text{ anions,} \\ 103 \text{ for } 4p \text{ anions, and } 146 \text{ for } 5p \text{ anions.} \quad (22)$$

We may then directly predict the properties of all of the corresponding compounds without further adjustment.

The generalization to lithium and beryllium compounds, with valence  $s$  shells but no  $p$  shells, would be quite immediate.  $\mu$  is determined from the  $1s$  core energy, and the factor 6 in Eq. (8) is replaced by a 2 for that ion. We would then need to see whether the same  $\eta_0$  values obtain. A similar generalization might be made to ten-electron compounds, such as  $\text{TlCl}$  and  $\text{PbO}$ , and to noble-metal halides. The generalization to compounds in the cesium-chloride structure would also be quite direct but has not been done. We therefore have not included compounds of Li, Tl, Pb, Cs, nor of the noble metals in our tabulations.

### C. The equilibrium spacing

We have directly minimized the sum of Eqs. (20) and (21) and evaluated the total and the second derivative with respect to  $d$  at the minimum. We look first at the values of  $d$  obtained. They are listed with experimental values (collected from standard sources in Ref. 1) in Table II. The general magnitudes are correct, and would even have been had we used the theoretical  $\eta_0 = 70.8$ ; in addition, the trends are rather well reproduced, particularly among the alkali halides. The accuracy does not compare well with that obtainable with ionic radii but, of course, use of an ionic radius for each ion allows so many adjustable

TABLE II. Predicted values, and experimental values in parentheses, of the nearest-neighbor distance, in angstroms, for rocksalt-structure compounds.

	F	Alkali halides		I
		Cl	Br	
Na	2.33 (2.13)	2.77 (2.81)	2.91 (2.99)	3.13 (3.24)
K	fit (2.67)	fit (3.15)	fit (3.30)	fit (3.53)
Rb	2.81 (2.82)	3.31 (3.29)	3.46 (3.45)	3.70 (3.67)
	O	Divalent compounds		Te
		S	Se	
Mg	2.15 (2.10)	2.62 (2.60)	2.76 (2.73)	
Ca	2.45 (2.41)	2.95 (2.85)	3.07 (2.96)	3.29 (3.18)
Sr	2.59 (2.58)	3.08 (3.01)	3.21 (3.12)	3.45 (3.24)
Ba	2.77 (2.76)	3.27 (3.19)	3.40 (3.30)	3.63 (3.49)
	ScN	Nitrides		LaN
		YN		
	2.46 (2.20)	2.58 (2.44)	2.75 (2.65)	

parameters (e.g., seven for the twelve alkali halides) that a very good fit is almost guaranteed. We have made no further adjustment in going to the divalent and trivalent compounds and so we may expect comparable success in going to other ionic compounds.

The semiquantitative success in moving to a new class of compounds such as the polyvalent compounds is important since we have abandoned the traditional view based upon Madelung energies. It is gratifying that the same representation of the electronic structure which allows elementary calculations of the electronic and dielectric properties also provides meaningful estimates of lattice distances.

#### D. Cohesion

We next consider the cohesive energy itself, the value of the sum of Eqs. (20) and (21) at the minimum; these are listed in Table III along with experimental values where we have them. The agreement is not as good for the alkali halides as obtained with Madelung energies and the difference between alkali ionization energy and halogen electron affinity; such predictions can be within half a volt or better depending upon what corrections are allowed. In fact the Madelung

TABLE III. Separation energy in electron volts, relative to isolated atoms predicted by Eqs. (20) and (21) (the magnitude of the energy at the minimum) and experimental values, in parentheses.  $\epsilon_s - \epsilon_p$  has been added for divalent compounds and  $\epsilon_s + \epsilon_d - 2\epsilon_p$  for trivalent compounds as appropriate.

	F	Alkali halides		I
		Cl	Br	
Na	15.33 (7.85)	10.11 (6.77)	8.90 (6.07)	7.45 (5.21)
K	14.81 (7.61)	9.81 (6.86)	8.67 (6.22)	7.32 (5.44)
Rb	14.66 (7.39)	9.73 (6.72)	8.59 (6.11)	7.27 (5.37)
	O	Alkaline earth dichalcogenides		Te
		S	Se	
Mg	20.87 (10.35)	12.05 (7.96)	10.33	
Ca	21.10 (11.03)	12.86 (9.69)	11.29 (7.33)	9.25
Sr	21.17 (10.44)	13.08 (9.26)	11.54	9.51
Ba	21.58 (10.29)	13.57 (9.35)	12.04 (10.31)	10.06
	ScN	Nitrides		LaN
		YN		
	18.15	20.55	21.54 (12.52)	

energy itself,  $-1.75e^2/d$  for alkali halides is a better estimate than ours; it is 9.42, 8.01, 7.64, and 7.13 eV, for example, for KF, KCl, KBr, and KI. However, the approach used here is also applicable to the polyvalent compounds where the Madelung approach seems to be quite inapplicable. The cohesion of the alkali halides is well documented and a theory which is restricted to them is not of such great value.

A further interesting point can be made concerning the separation energy. Because the overlap interaction rises quite abruptly, its contribution in reducing the separation energy is much smaller than the band-structure term and  $\delta E_{\text{band}}$  of Eq. (20) alone becomes an estimate of the separation energy for the alkali halides.  $V_2$  is small compared to  $V_3$  so this is approximately  $\epsilon_s - \epsilon_p$ . Furthermore, for a nearest-neighbor calculation of the bands in the rocksalt structure, based upon only anion  $p$  states and cation  $s$  states, the band gap itself is given by  $\epsilon_s - \epsilon_p$ . Thus in addition to giving predictions of each of these numbers the theory suggests that the two experimental quantities should be approximately equal, in accord with experiment. The same argument



would say that the separation energy for the divalent compounds should be approximately twice the band gap, again in rough accord with experiment. It provides a simple, plausible rule of thumb.

#### E. Bulk modulus and elasticity

Finally we evaluated the second derivative of the sum of Eqs. (20) and (21) with respect to  $d$  at the minimum and obtained the bulk modulus  $B = -(1/18d)\partial^2 E/\partial d^2$ . The results are given in Table IV along with some experimental values. The prediction is quite sensitive to the value of  $d$  at the minimum and the values obtained with the HP25 may have several percent error. In contrast to the energy of separation, this quantity is dominated by the overlap interaction and the extent of the agreement with experiment supports the form we have used and the four coefficients  $\eta_0$  adjusted to give the spacing in the potassium halides. The extent of the agreement in the potassium halides would suggest that quite good values might be obtained if  $\eta_0$  were adjusted for each compound to obtain the observed crystal spacing rather than using universal values. That would seem a better approach for actual predictions of properties but not for testing our representation of the electronic structure, which is the purpose here.

TABLE IV. Predicted bulk modulus, and experimental values in parentheses, for rocksalt-structure compounds. Values are in  $10^{11}$  ergs/cm<sup>3</sup>.

	F	Alkali halides		I
		Cl	Br	
Na	7.0 (4.65)	3.8 (2.40)	3.2 (1.99)	2.5 (1.51)
K	2.7 (3.05)	1.6 (1.74)	1.40 (1.48)	1.2 (1.17)
Rb	1.95 (2.62)	1.1 (1.56)	1.0 (1.30)	0.8 (1.06)
	O	Divalent compounds		Te
		S	Se	
Mg	13.4 (15.3)	6.2	4.9	
Ca	6.0 (10.7)	3.2	1.5	1.91
Sr	4.1	2.3	2.0	1.53
Ba	2.5	1.7	1.4	1.09
	ScN	Nitrides		LaN
		YN		
	6.8	5.2	3.43	

The calculation of the other elastic constants is not so immediate. Second-neighbor repulsive interactions between anions have been included which stabilizes the lattice under shear. However, the distortion of the lattice distorts the Brillouin zone and new special points are required for the evaluation of the band energy. Equation (20) suggests an appropriate form: The coupling between neighbors enters through  $nV_{sp\sigma}^2$ , where  $n$  is the number of neighbors and  $V_{sp\sigma}$  depends upon  $d$ . We write this as a sum of terms for the six neighbors and evaluate each for the nearest-neighbor distance in the distorted crystal. This is indeed consistent with second-order perturbation theory and therefore a direct generalization of the method used to obtain Eq. (20). Thus this method may be used for a strain  $e_1 = \partial u_x/\partial x$  to evaluate  $c_{11}$  and in combination with our value of the bulk modulus  $B = (c_{11} + 2c_{12})/3$  we obtain two of the elastic constants,  $c_{11}$  and  $c_{12}$ . The total energy under distortion is obtained from Eq. (20) [with  $nV_{sp\sigma}^2$  replaced by a sum over neighbors  $j$  at  $\vec{d}_j$ , that is,  $\sum_j V_{sp\sigma}^2(d_j)$ ] and Eq. (21). The values of these two elastic constants for four alkali halides (experimental and theoretical values for compounds involving K, Cl, and Br should vary smoothly between these limits) are listed in Table V; values are also given for MgO, for which we have experimental values.

The predicted rigidity ( $c_{11} - c_{12}$  for a pure shear) is slightly less accurately predicted than the bulk modulus, but not significantly so. Further, the accuracy is not very much less than values obtained with the Madelung energy alone. The electrostatic values of  $c_{12}$  for the five compounds listed in Table V are 2.77, 0.73, 1.27, 0.44, and 16.2, respectively. (See, for example, Ref. 1, p. 313.) It is remarkable indeed that similar

TABLE V. Predicted elastic constants, and experimental values in parentheses, for rocksalt-structure compounds. Values are in  $10^{11}$  ergs/cm<sup>3</sup>.

	$c_{11}$	$c_{12}$	$c_{44}$
NaF	14.39 (9.7)	3.31 (2.44)	3.48 (2.81)
NaI	4.21 (3.03)	1.65 (0.89)	1.71 (0.73)
RbF	4.93 (5.52)	1.94 (1.40)	1.97 (0.95)
RbI	1.97 (2.56)	0.22 (0.36)	0.23 (0.28)
MgO	17.7 (29.2)	11.25 (9.1)	11.53 (15.4)

agreement with experiment for the elasticity is obtained assuming such different physical origins for the rigidity just as the two very different views of cohesion each gave a semiquantitative account of experiment.

Use of this same generalization for the calculation of  $c_{44}$  leads to a value equal to  $c_{12}$  since  $c_{44} = c_{12}$  is one of the Cauchy relations for a system in equilibrium under the influence of central-force interactions alone.<sup>14</sup> However, direct application of fourth-order perturbation theory in  $V_{sp\sigma}$  gives angular terms in  $c_{44}$ , called the chemical grip<sup>15</sup>; these are not present in the generalization of Eq. (20) described above. These angular terms entering  $c_{44}$  (but not  $c_{11} - c_{12}$ ) are given by

$$\delta E_{\text{grip}} = \frac{4V_{sp\sigma}^4}{E_g^3} \sum_{j>i} \cos^2 \theta_{ij}. \quad (23)$$

(Equation 19–29 in Ref. 1 was in error by a factor of two in the first printing.) Under the strain  $e_4$  four angles between neighbors to each anion are changed to  $\frac{1}{2}\pi \pm e_4$  and, with an anion density of  $4/(2d)^3$ , this gives a contribution to  $c_{44}$  of

$$\delta c_{44} = \frac{16V_{sp\sigma}^4}{d^3 E_g^3}. \quad (24)$$

[This corresponds to Eq. (19–32) of Ref. 1, twice as large as the expression in the first printing, and with  $E_g$  entering explicitly rather than from the approximate relation  $E_g = 9.1\hbar^2/md^2$  used in Ref. 1.] For  $E_g$  we use the expression  $[(\epsilon_s - \epsilon_p)^2 + 24V_{sp\sigma}^2]^{1/2}$  corresponding to the special point in the Brillouin zone, as in Eq. (20). These small corrections, giving deviations from the Cauchy relations, have been added giving the  $c_{44}$  values listed in Table V. It may not be surprising that they are not so accurately given since they are of fourth order in the coupling  $V_{sp\sigma}$ .

#### F. Coupling between full and empty states

In using the overlap interaction based upon occupied states in the closed-shell system we are assuming that this is the dominant term in the repulsion. There are additional repulsive terms arising from the  $SV_{sp\sigma}$  term of Eq. (5) from the coupled anion occupied  $p$  states and cation unoccupied  $s$  states. The success of the predictions given in Tables II, III, IV, and V would suggest that these terms are small. We shall consider these terms using EHT in Sec. VII. As the valence difference increases this must ultimately fail. If, for example, we consider the isoelectronic series of diatomic molecules, NaCl, MgS, AlP, Si<sub>2</sub>, from this point of view we would be describing the Si-Si overlap interaction as arising from the  $2p$  electrons on the first silicon with the  $3p$  electrons on the second but not in-

cluding the interaction between the  $3p$  on the first and the  $2p$  on the second, which makes no sense. We shall see the resolution of this difficulty as we now consider covalent solids.

## VI. COVALENT SOLIDS

Both the band-structure energy [Eq. (20) for ionic solids] and the overlap energy [Eq. (21) for ionic solids] change fundamentally in the covalent solids (such as germanium and the compounds GaAs, ZnSe, CuBr isoelectronic with it). Each atom is tetrahedrally coordinated and the occupied electronic states are appropriately thought of as bond orbitals in the four bonds per atom pair rather than anion  $s$  and  $p$  states; the latter, as we have seen, makes no sense at all in the elemental semiconductors where there is no distinction between anions and cations.

### A. The band-structure energy

The bond orbital model is perhaps the simplest formulation of the band-structure energy of such systems.<sup>1</sup> Starting again from isolated atoms we first form  $sp^3$  hybrids of the  $s$  and  $p$  states, oriented along the four nearest-neighbor directions. The energy of each is  $\epsilon_h = (\epsilon_s + 3\epsilon_p)/4$  so that transferring the electrons from the atomic configuration,  $s^2p^2$  for germanium, into four hybrid states requires a *promotion energy* of  $\epsilon_p - \epsilon_s$ ; a slightly more complicated expression arises in the compound semiconductors.<sup>1</sup> All interatomic matrix elements are then neglected except between the two hybrids directed into each bond. That matrix element may be evaluated as<sup>1</sup>

$$-V_2^h = (V_{ss\sigma} - 2\sqrt{3}V_{sp\sigma} - 3V_{pp\sigma})/4 = -4.37\hbar^2/md^2. \quad (25)$$

$V_2^h$  is called the hybrid covalent energy and plays exactly the role of the  $V_2$  introduced in Sec. II. In elemental semiconductors the energy of the bond orbital arising from the two coupled hybrids is  $\epsilon_h - V_2^h$ . In the compound semiconductors the two hybrid energies differ and a hybrid polar energy,  $V_3^h = (\epsilon_h^c - \epsilon_h^a)/2$ , is defined in terms of their difference. Then the bond energy becomes  $\frac{1}{2}(\epsilon_h^c + \epsilon_h^a) - (V_2^h + V_3^h)^{1/2}$ . The total band-structure energy becomes the promotion energy to transfer the electrons to  $sp^3$  hybrid states plus the bond formation energy from converting these to bond states. (Ref. 1, pp. 169, 170).

### B. The overlap interaction

The overlap interaction is also modified. We may imagine first placing the electrons in hybrid orbitals and then bringing the atoms together with an energy of repulsion arising when the electron

distributions overlap. Harrison and Sokel<sup>3</sup> carried out a calculation of the resulting overlap interaction exactly as described in Sec. III, but using an electron density corresponding to the four electrons per atom in  $sp^3$  hybrids rather than eight electrons in a closed-shell configuration (either  $s^2p^6$  or eight electrons in  $sp^3$  hybrids, which are equivalent). This gave too small an overlap repulsion, and therefore predicted too small an internuclear distance.

The situation was in fact worse than they realized (Ref. 1, p. 171). They used a covalent energy  $V_2 = 1.8\hbar^2/md^2$ , obtained from the optical absorption peak  $E_2$ , rather than the  $4.37\hbar^2/md^2$  which we obtained from the universal parameters. (Those universal parameters also predict an absorption peak  $E_2$  corresponding to  $V_2 = 2.16\hbar^2/md^2$  in rough agreement with experiment; at that time it was not recognized that different covalent energies were needed for bonding and dielectric properties.) Use of the hybrid covalent energy would considerably worsen their agreement with experiment.

They recognized, however, that their calculated overlap interaction was in serious error and attributed this to the application of the density-functional formalism to a system which was not in the electronic ground state. We may both see that this conjecture was correct and see how to rectify it by returning to the LCAO formulation of Sec. II. The evaluation of energy levels given there remains valid independent of the occupation of those levels. Equation (5) gives the energy levels and, for interaction between identical atoms, gives

$$\frac{\langle \psi_i | H | \psi_i \rangle}{\langle \psi_i | \psi_i \rangle} = \epsilon_\alpha + \delta\epsilon_\alpha \pm V_2^h + S V_2^h. \quad (26)$$

For the closed-shell system we have discussed up until this section, the  $\pm V_2^h$  for the interaction between the closed shells cancels and the overlap interaction, dominated by the kinetic energy, corresponds to the term  $S V_2^h$  multiplied by the number of electrons. This is the energy we estimated using the density-functional formalism in Sec. III. If only half of those orbitals were occupied,  $S$  and  $V_2^h$  would retain the same meanings but there would be only half as many electrons and the overlap interaction would be reduced by a factor of two. Thus the correct estimate of the overlap interaction in the half-filled shell (such as germanium) is obtained by carrying out the calculation of electronic kinetic energy using twice the atomic electron density and dividing the result by two.

Note that this *is not equivalent to the procedure used by Harrison and Sokel*. They used half the

closed-shell density but since the kinetic energy is proportional to  $n(\vec{r})^{5/3}$  this gave a repulsion  $\frac{1}{2}^{5/3}$  as large as the closed-shell repulsion. Thus we should multiply the Harrison-Sokel kinetic energy term by  $2^{5/3}$  and then divide by two, scaling up their kinetic energy term by a factor of  $2^{2/3}$ . The result of doing this for silicon is shown in Fig. 2. The increase in overlap interaction is very large indeed since in the earlier calculation the kinetic energy was very nearly canceled by the exchange energy so that the corrected curve is very nearly equal to the added kinetic energy,  $(2^{2/3} - 1)$  times the original kinetic energy.

We may use this correction to the overlap interactions calculated by Harrison and Sokel for C, Si, and Ge, replace their covalent energy by the hybrid covalent energy, and again predict the equilibrium spacing, cohesion, and bulk modulus. This gives predictions roughly in accord with experiment for silicon and germanium as seen from the values in Table VI. A similar calculation for diamond gave an equilibrium spacing less than half the observed value and was not included in the table. Note that these predictions are entirely from first principles; no adjustment of parameters has been made. Thus we may conclude the largest error of the earlier treatment has been corrected though the predictive value is still limited.

#### C. Approximate form for homopolar semiconductors

We may also approximate the overlap interaction by the analytic form for the excess kinetic energy derived in Sec. III:

$$V_0(d) = -\eta_0 \epsilon_p \mu_h d e^{-5\mu_h d/3} \quad (27)$$

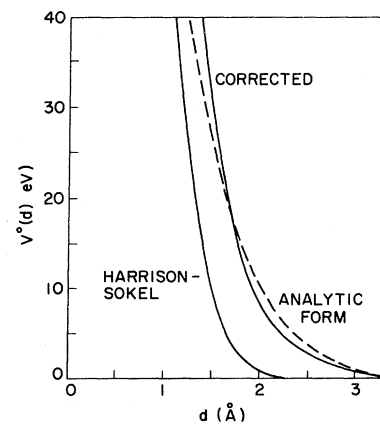


FIG. 2. The overlap interaction for silicon obtained by Harrison and Sokel (Ref. 2) and with the kinetic energy contribution corrected for open-shell systems. The dashed line is the analytic form  $-\eta_0 \epsilon_p \mu_h d e^{-5\mu_h d/3}$  with  $\eta_0 = 56.7$  and  $\hbar^2 \mu_h^2 / 2m = -(\epsilon_s + 3\epsilon_p) / 4$ .

TABLE VI. Predicted properties of silicon and germanium based upon the band-structure energy  $-2V\frac{1}{2}$  per bond, the promotion energy  $(\epsilon_p - \epsilon_s)/2$  per bond, and the corrected overlap interaction of Fig. 2. Experimental values are in parentheses.

	Bond length (Å)	Cohesion (eV/bond)	Bulk modulus ( $10^{12}$ ergs/cm <sup>3</sup> )
Si	2.22 (2.35)	4.67 (2.32)	1.4 (0.99)
Ge	2.71 (2.45)	2.51 (1.94)	0.91 (0.77)

Use of a value of  $\mu$  determined from the valence-band  $p$  state is found to give too soft a repulsion. This may not be surprising since at the close spacing appropriate to covalent solids the more compact  $s$  states are far from negligible. We partially compensate for this by using a hybrid  $\mu$  determined from  $-\epsilon_h = \hbar^2 \mu_h^2 / 2m$  which fits well with the analysis of the band-structure energy in terms of hybrid orbitals rather than  $p$  states. We then adjusted  $\eta_0$  to give the observed internuclear distance for C, Si, Ge, and Sn (listed in Table VII) and used these parameters to predict the cohesion and bulk modulus for these four semiconductors. The results are given in Tables VIII and IX. Again the agreement with experiment is reasonable.

It is of interest to note that, as in the ionic solids, the adjusted  $\eta_0$  values are not greatly different from the predicted value ( $\eta_0 = 47$  for four

TABLE VII. Predicted internuclear distance in angstroms, based on the overlap interaction of Eq. (31) and an energy per bond of  $-2(V\frac{1}{2} + V\frac{1}{3})^{1/2}$ . The same coefficient  $\eta_0$  is used for all compounds in the same row. Experimental distances are given in parentheses.

	C	BN	BeO	
$\eta_0 = 45.5$	fit	1.57	1.90	
	(1.54)	(1.57)	(1.65)	
	Si	AlP	MgS	
	$\eta_0 = 56.7$	fit	2.36	2.49
	(2.35)	(2.36)		
	Ge	GaAs	ZnSe	CuBr
	$\eta_0 = 60.9$	fit	2.45	2.53
	(2.44)	(2.45)	(2.45)	(2.49)
	Sn	InSb	CdTe	AgI
	$\eta_0 = 73.4$	fit	2.81	2.89
	(2.80)	(2.81)	(2.81)	(2.80)

TABLE VIII. Predicted separation energy in electron volts per bond relative to isolated atoms. Values are for the  $\eta_0$  and for the predicted spacings of Table VII. Experimental values are in parentheses.

C	BN	BeO	
7.21 (3.68)	6.90 (3.34)	5.56 (3.06)	
Si	AlP	MgS	
3.49 (2.32)	3.64 (2.13)	3.39	
Ge	GaAs	ZnSe	CuBr
2.73 (1.94)	2.79 (1.63)	2.56 (1.29)	2.20 (1.45)
Sn	InSb	CdTe	AgI
2.17 (1.56)	2.25 (1.40)	2.11 (1.03)	1.88 (1.18)

electrons per atom rather than 70 for six  $p$  electrons). It is also of interest to plot the silicon overlap interaction with  $\eta_0 = 56.7$ ; it is compared with the corrected first-principles form in Fig. 2. Even with the use of  $\mu$  based upon the hybrid energy the repulsion is softer than the corrected first-principles calculation by Harrison and Sokel. This is reflected in the predicted bulk modulus being too small.

#### D. Polar semiconductors

In order to treat polar semiconductors we must again make an identification between the overlap interaction and the nonorthogonality terms of LCAO theory. Using the hybrid matrix elements for covalent solids, and the energy levels of Eq.

TABLE IX. Predicted bulk modulus (in  $10^{12}$  ergs/cm<sup>3</sup>) from the calculation leading to Tables VII and VIII. Experimental values are in parentheses.

C	BN	BeO	
0.31 (4.46)	0.18	0.40	
Si	AlP	MgS	
0.67 (0.98)	0.53	0.23	
Ge	GaAs	ZnSe	CuBr
0.65 (0.76)	0.54 (0.75)	0.29 (0.60)	0.14
Sn	InSb	CdTe	AgI
0.43	0.36 (0.46)	0.20 (0.42)	0.11

(5) (dropping the shifts  $\delta\epsilon$  of the term values) we write the terms in the energy per bond which depend upon distance as

$$\delta E_{\text{tot}} = -2(V_2^h + V_3^h)^{1/2} + 2SV_2^h. \quad (28)$$

The predicted equilibrium spacing is at the minimum of this energy as a function of  $d$ . In order to determine that minimum we must know the dependence of  $S$  upon  $d$ . An approximate analysis of the integrals involved, which will be given in Sec. VII, will suggest that both  $S$  and  $V_2^h$  should be proportional to  $e^{-\mu d}$  and thus that  $S$  should vary as  $d^{-2}$  near the equilibrium spacing just as  $V_2^h$  does. Then we may immediately take the derivative of Eq. (28) with respect to  $d$  and set it equal to zero to obtain

$$d\delta E_{\text{tot}}/\partial d = 4V_2^h/(V_2^h + V_3^h)^{1/2} - 8SV_2^h = 0. \quad (29)$$

This equation would be used to predict the equilibrium  $d$ . However, it is interesting to note its consequence concerning  $S$ . We may solve Eq. (29) for  $S$  at the equilibrium spacing to obtain

$$S = \frac{1}{2}V_2^h/(V_2^h + V_3^h)^{1/2} \equiv \frac{1}{2}\alpha_c^h,$$

where

$$\alpha_c^h = V_2^h/(V_2^h + V_3^h)^{1/2} \quad (30)$$

is called the hybrid covalency.<sup>1</sup> For homopolar semiconductors ( $V_3^h = 0$ ) this predicts  $S = \frac{1}{2}$  at the equilibrium spacing, in accord with evaluations made in terms of real atomic orbitals. [See, for example, Eq. (5), Ref. 4.]

This is a remarkable confirmation of the equivalence of the  $2SV_2^h$  term and the overlap interaction  $V_0(d)$  for homopolar semiconductors. However, Eq. (30) indicates that  $S$  drops significantly in a series of increasing polarity such as Ge, GaAs, ZnSe, CuBr, whereas the analysis in Sec. VII will suggest  $S$  to be independent of the polarity, at least if the equilibrium spacing remains the same. The only way this could be consistent with Eq. (30) would be if the lattice distance increased significantly with polarity in such a series, a trend which is not exhibited by the observed spacing.

It is not difficult to see where the difficulty has arisen. For a highly polar material we could expand the first term in Eq. (28) in  $V_2^h$ , obtaining the leading term in the attraction between atoms proportional to  $V_2^h$  or  $d^{-4}$ . But if  $S$  varies as  $d^{-2}$  then the second term, the repulsion, is also proportional to  $d^{-4}$ . This similar dependence leads to instability; the attractive and repulsive forces (both proportional to  $d^{-5}$ ) must be equal and opposite at the equilibrium spacing but they also very nearly cancel over a considerable

range of  $d$  and small terms, which we could neglect in other systems, become important. Perhaps an analogous calculation led to the poor prediction of equilibrium spacing in diamond based upon the corrected Harrison-Sokol overlap interaction in Section VI B and for our finding too soft an overlap interaction in the homopolar semiconductors.

This difficulty did not arise in ionic solids where the repulsion came from deep levels (including a core level on the metallic atom) and was quite abrupt in comparison to the attractive interactions arising from valence levels. We dropped the much softer repulsions arising from the valence electrons.

We see that the overlap interaction in covalent solids is a much more sensitive problem. The empirical fact is that the internuclear distance does not vary greatly with polarity though the attractive force in the bond orbital model drops with decreasing covalency. The empirical consequence is that the overlap interaction must drop as  $\alpha_c^h$  in such a series so we may take

$$V_0(d) = \eta_0 \alpha_c^h (\hbar^2/2m) \bar{\mu}_h^3 d e^{-5\mu_h d/3}, \quad (31)$$

with coefficient  $\eta_0$  constant in an isoelectronic series. This will give reasonable results but we should recognize that an empirical inclusion of a factor of  $\alpha_c^h$  has been required. We retain the result, to be obtained in Sec. VII, that  $S$  is constant at approximately  $\frac{1}{2}$  in such an isoelectronic series of covalent solids though this is not strictly consistent with identifying the overlap interaction Eq. (31) with the LCAO counterpart  $2SV_2$ . We also note that rather different approximations in ionic and covalent solids have been required. The change in crystal structure from one set to the other seems to provide a suitable dividing line between the two outlooks. However, since we use different approximations for the two structures we cannot compare the energies between the two structures.

We may make an immediate application of Eq. (31) to the compound semiconductors. We include the promotion energy for the compound and the bonding energy given by  $-2(V_2^h + V_3^h)^{1/2}$  rather than the  $-2V_2^h$  appropriate to the homopolar semiconductors. There are too many semiconductor systems for a complete survey but a tabulation for the compounds isoelectronic with C, Si, Ge, and Sn will be sufficient. Tables VII, VIII, and IX give the predicted equilibrium spacing, cohesive energy, and bulk modulus for these compounds obtained without the introduction of any additional parameters.

From Table VII it is seen that the theory predicts too large an increase in  $d$  with polarity;

in detail this arises from the average  $\mu_h$  for a compound being considerably smaller than the value of  $\mu_h$  for the homopolar semiconductor isoelectronic with it. The predicted cohesive energy, given in Table VIII, is large, as it was in the ionic compounds, and by a similar ratio. Again the trends from material to material are rather well given. The predicted bulk modulus, given in Table IX, is too small, reflecting the softness of the approximate overlap interaction which we discussed for the homopolar semiconductors, but the experimental trends are reproduced. In summary, use of Eq. (31) for the overlap interaction, with an  $\eta_0$  value depending only upon row in the periodic table, gives a reasonable account of the cohesive properties of the tetrahedral semiconductors but any quantitative fit requires introduction of additional adjustable parameters such as an  $\eta_0$  value chosen for each compound.

An interesting and more elementary theory of the spacings can be derived directly from our identification of the nonorthogonality term  $2SV_2^h$ , with the overlap interaction of Eq. (31). Noting again the variation of  $S$  as  $d^{-2}$  we may evaluate the derivative of this energy to obtain  $\partial \ln(2SV_2^h)/\partial \ln d = -4$ . The corresponding expression obtained from Eq. (31) (with  $\alpha_c^h$  a constant for each material as assumed before) gives  $\partial \ln V_0/\partial \ln d = 1 - 5\bar{\mu}_h d/3$ . Requiring that both be valid near the equilibrium spacing gives immediately

$$d = 3/\bar{\mu}_h. \quad (32)$$

This is a direct prediction, without parameters, of  $d$  in terms of the term values of the constituent atoms. Its comparison with experiment is given in Table X and confirms it as a meaningful rule of thumb.

TABLE X. Equilibrium spacings in angstroms, obtained from the average hybrid parameter  $d = 3/\bar{\mu}_h$ . Experimental values are in parentheses.

C	BN	BeO		
1.76 (1.54)	1.76 (1.57)	1.80 (1.65)		
Si	AlP	MgS		
2.04 (2.35)	2.04 (2.36)	2.10		
Ge	GaAs	ZnSe	CuBr	
2.02 (2.44)	2.03 (2.45)	2.07 (2.45)	2.12 (2.49)	
Sn	InSb	CdTe	AgI	
2.13 (2.80)	2.14 (2.81)	2.17 (2.81)	2.22 (2.80)	

## VII. IDENTIFICATION WITH EXTENDED HÜCKEL THEORY

Finally we may identify the approximations which we have made with the familiar EHT of quantum chemistry as given by Hoffmann.<sup>16</sup> This method is also based upon an LCAO formalism but utilizes real atomic orbitals, or an expansion of them in Slater orbitals. It is convenient to specify the EHT prescription in terms of pairs of orbitals as we did in Sec. II.

### A. Extended Hückel theory

The one-electron state is again written as a linear combination of the two orbitals, as in Eq. (1), and the energy written again as in Eq. (3). The variational method leads again to the equations

$$H_{\alpha\alpha}u_{i\alpha} + H_{\alpha\beta}u_{i\beta} - \epsilon_i u_{i\alpha} - \epsilon_i S u_{i\beta} = 0, \quad (33)$$

$$H_{\beta\alpha}u_{i\alpha} + H_{\beta\beta}u_{i\beta} - \epsilon_i S u_{i\alpha} - \epsilon_i u_{i\beta} = 0.$$

The solution of these leads exactly to Eq. (5) with parameters defined in Eq. (4). However, in the EHT the parameters are evaluated differently. The overlap  $S = \langle \beta | \alpha \rangle$  is evaluated explicitly in terms of the atomic orbitals. Then  $H_{\alpha\alpha}$  and  $H_{\beta\beta}$  are taken to be the ionization energies of the atoms, corresponding to our choice  $\epsilon_\alpha$  and  $\epsilon_\beta$ , but dropping the shifts  $\delta\epsilon_\alpha$  and  $\delta\epsilon_\beta$ , as we in fact did when we used only the kinetic energy contribution to the overlap interaction. The off-diagonal matrix elements in EHT are then taken as

$$H_{\alpha\beta} = \frac{1}{2}K(\epsilon_\alpha + \epsilon_\beta)S, \quad (34)$$

with  $K$  taking the empirical value 1.75. This choice of parameters, rather than the universal parameters [Eq. (19)] is a principal difference in the two approaches.

In EHT one then approximates the total energy by the sum of occupied orbital energies  $\epsilon_i$ . This is in fact equivalent to dropping the terms in  $\delta\epsilon_\alpha$  and  $\delta\epsilon_\beta$  and identifying  $SV_2$  as the overlap interaction. Thus we see that this assumption used in EHT, which at first seems quite inappropriate, is justified because the bonding-antibonding shifts  $\pm V_2$  are not affected greatly by self-energy corrections nor is the overlap interaction since it is principally kinetic energy. Our neglect of the contribution of the coupling between full and empty states in ionic compounds is an approximation made in the density-functional approach, but is not made in EHT if both orbitals are included in the basis set. The corresponding terms have been included in our analysis of covalent solids where the coupling of all orbitals in the basis set are included in the overlap interaction.

### B. Application to covalent solids

Because EHT also gives reasonable predictions of properties, the parameters in the two theories which we have identified with each other are also expected to have similar values. We may confirm this with an approximate evaluation of the overlap  $S$  using the asymptotic form for the wave function  $R_l(r) = (\mu^3/\pi)^{1/2} e^{-\mu r}$ , from normalization of Eq. (6) again with  $\gamma=0$ . If we ignore any angular dependence the overlap integral becomes of the form of that in Eq. (17) and may be evaluated exactly as follows:

$$S = e^{-\mu d} (1 + \mu d + \mu^2 d^2 / 3). \quad (35)$$

Equation (32) gave the approximate value of  $\mu_h d = 3$  at the observed spacing for covalent solids, from which  $S = 0.35$ , in rough accord with the value 0.5 from the bond orbital model for homopolar semiconductors. This expression also gives  $(1/S)d\partial S/\partial d = -12/7$  at  $\mu_h d = 3$ , comparable to the value  $-2$  for an inverse-square dependence. Thus Eq. (35) also gives close to a  $d^{-2}$  dependence to the interatomic matrix elements  $-V_2$ . In fact, using  $\mu_h d = 3$  and the hybrid energy for silicon in Eq. (34) gives  $V_2^h = 5.05$  eV, comparable to the value 6.03 eV from universal parameters, Eq. (25).

The overlap interaction in EHT becomes

$$V_0(d) = 2SV_2^h = 3.5 \epsilon_h [1 + \mu_h d + (\mu_h d)^2 / 3]^2 e^{-2\mu_h d}. \quad (36)$$

The exponent is  $-2\mu_h d$ , close to the  $-5\mu_h d/3$  from local-density theory. The actual value for silicon from Eq. (36) at  $\mu_h d = 3$  is 3.52 eV, comparable to the value of  $V_0(d) = 5.05$  eV from Eq. (27). [These figures are sensitive to the choice of  $\mu_h d$ . Equation (27) gives 9.49 eV if  $\mu_h d$  is taken as 3 rather than as the value 3.46 obtained from the term values and the equilibrium spacing.]

The behavior of the parameters for polar materials requires the evaluation of  $S$  with  $\mu_1 \neq \mu_2$ . Formulas for the values of such integrals have been given by Sahni and Cooley.<sup>17</sup> If we define a difference parameter

$$\tau = (\mu_1 - \mu_2) / (\mu_1 + \mu_2), \quad (37)$$

use the asymptotic form as in Eq. (35), and neglect angular dependence, their formulas yield

$$S = (1 - \tau^2)^{3/2} \left( (1 + \bar{\mu}d - \tau^2) \frac{\sinh \bar{\mu}d\tau}{\bar{\mu}d\tau} + \tau^{-2} \cosh \bar{\mu}d\tau \right) e^{-\bar{\mu}d}, \quad (38)$$

which reduces to Eq. (35) as  $\tau$  approaches zero. It is, of course, even in  $\tau$  and is quite insensitive to  $\tau$  at the observed spacings where  $\bar{\mu}d$  is near 3; in fact the quadratic term in  $\tau$  vanishes when

$\bar{\mu}d = 3.2$  and it only varies by a few percent over the range of  $\tau$ 's which occur in the polar semiconductors. This result, combined with Eq. (34), is consistent with our taking  $V_2$  as independent of polarity but would not suggest the strong dependence of the overlap interaction on covalency in polar semiconductors implied by Eq. (31). The cancellation which may be responsible for that discrepancy was discussed just before that equation.<sup>18</sup>

### C. Application to ionic solids

The same numerical comparison of terms may also be made for ionic solids. An evaluation of the overlap  $S$  of the cation  $s$  state and anion  $p$  state for KCl from Eq. (38) gives 0.16, slightly larger than the 0.14 obtained from Eq. (36). EHT then would give [Eq. (34)] an  $sp$  matrix element of 2.35 eV, comparable to the 1.41 eV from universal parameters. However, the overlap interaction  $2SV_2$  arising from coupling between empty cation  $s$  states and full anion  $p$  states which this yields, 0.77 eV at the internuclear distance of KCl, is much too large to be neglected as we did in using only occupied states in Eq. (21); in fact, it is considerably larger than the 0.13 eV for the overlap interaction we used. On the other hand, a  $2SV_2$  interaction similarly constructed on the basis of the occupied cation  $p$  state and occupied anion  $p$  state is 0.06 eV of the correct general size.

This would suggest that EHT would not have given reasonable spacings for this system if we had included the repulsion  $2SV_2$  associated with valence states and had not included any Madelung terms. This may not be surprising. When we assumed that the charge distribution does not change appreciably in transferring electrons from potassium  $s$  states to chlorine  $p$  states at the observed spacing, we assumed that the orbitals essentially span the same space, consistent with an  $S = 0.16$  for each of the six neighbors. Such a situation has not been carefully formulated but it is not clear that the  $2SV_2$  repulsive term *should* apply there.

### D. Summary

The two seemingly quite different approaches, EHT and ours, are remarkably consistent, particularly for covalent solids. Identifying the two theories, in fact, can give a number of quantitative predictions which are valid on the scale of the agreement found in the last paragraphs. We prefer the universal parameter theory because the evaluation of matrix elements from Eq. (19)

is immediate and allows analytic formulas for the various bonding and dielectric properties. Recall that EHT evaluations require numerical evaluation of three-dimensional integrals if the

simplifying approximations leading to Eqs. (35) and (38) are not made. Once one is forced to numerical procedures there is little reason not to move on to more accurate numerical methods.

<sup>1</sup>W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).

<sup>2</sup>R. G. Gordon and Y. S. Kim, *J. Chem. Phys.* **56**, 3122 (1972).

<sup>3</sup>W. A. Harrison and R. Sokel, *J. Chem. Phys.* **65**, 379 (1976).

<sup>4</sup>W. A. Harrison and S. Ciraci, *Phys. Rev. B* **10**, 1516 (1974); see also Appendix B, Ref. 1.

<sup>5</sup>V. K. Nikulin, *Zh. Tekh. Fiz.* **41** (No. 1), 41 (1971) [*Sov. Phys.—Tech. Phys.* **16** (No. 1), 28 (1971)]; V. K. Nikulin and Yu. N. Tsarev, *Chem. Phys. (Netherlands)* **10**, 433 (1975).

<sup>6</sup>See, for example, Ref. 1.

<sup>7</sup>C. F. Fischer, *At. Data* **4**, 301 (1972).

<sup>8</sup>S. Froyen and W. A. Harrison, *Phys. Rev. B* **20**, 2420 (1979). This is also discussed in Ref. 1. L. F. Mattheiss (private communication) has subsequently pointed out an error in the analysis for tetrahedral systems. The  $\Gamma_{15}$  conduction-band level should have been identified with the free-electron band at  $(9\pi^2/8)(\hbar^2/md^2)$  rather than  $(3\pi^2/2)(\hbar^2/md^2)$ . It approaches this value as the pseudopotential is turned off. This correction does not modify the predicted  $V_{ss\sigma}$  nor  $V_{pp\sigma}$ , but reduces  $V_{pp\sigma}$  by a factor of 2 and modifies

$V_{sp\sigma}$  slightly. Use of such matrix elements would eliminate the band gap; thus the adjustment of matrix elements to known bands, discussed in Ref. 1, Ref. 8, and here, is more essential than Froyen and Harrison realized.

<sup>9</sup>W. A. Harrison, *Bull. Am. Phys. Soc.* **21**, 1315 (1976).

<sup>10</sup>F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, 1964); also listed in Ref. 1.

<sup>11</sup>See, for example, R. C. Chaney, E. E. Lafon, and C. C. Lin, *Phys. Rev. B* **4**, 2734 (1971).

<sup>12</sup>Joel Brock, private communication.

<sup>13</sup>A. Baldereschi, *Phys. Rev. B* **7**, 5212 (1973); discussed also in Ref. 1.

<sup>14</sup>See, for example, M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1954).

<sup>15</sup>Reference 1, p. 459ff.

<sup>16</sup>R. Hoffmann, *J. Chem. Phys.* **39**, 1397 (1963).

<sup>17</sup>R. C. Sahni and J. W. Cooley, NASA Technical Note D-146, Technical Information Division, Code BID, National Aeronautics and Space Administration, Washington 25, D.C. (unpublished).

<sup>18</sup>The discrepancy is discussed in Ref. 1, 188ff.